



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : H01M 12/06	A1	(11) International Publication Number: WO 93/12554 (43) International Publication Date: 24 June 1993 (24.06.93)
(21) International Application Number: PCT/US92/10817 (22) International Filing Date: 14 December 1992 (14.12.92) (30) Priority data: 809,196 16 December 1991 (16.12.91) US (60) Parent Application or Grant (63) Related by Continuation US 809,196 (CIP) Filed on 16 December 1991 (16.12.91) (71) Applicant (for all designated States except US): MATSI, INC. [US/US]; 430 Tenth Street N.W., Ste. S007, Atlanta, GA 30318 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : MERRY, Glenn, W. [US/US]; 1280 West Peachstreet N.W., Apartment 3906, Atlanta, GA 30367 (US). PUTT, Ronald, A. [US/US]; 803 Saddle Hill, Marietta, GA 30068 (US). (74) Agents: WEAVER, Jeffrey, K. et al.; Townsend and Townsend, One Market Plaza, 20th Fl., Steuart Tower, San Francisco, CA 94105 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, RO, RU, SD, SE, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published With international search report.
(54) Title: COLLAPSING FOAM ANODE BACKING FOR ZINC-AIR BATTERY		
(57) Abstract		
<p>A metal-air cell (70), such as is used in a zinc-air battery, includes a tray (2) having one or more air holes (3) and a hydrophobic membrane (4) covering the air holes (3). A substantially flat air electrode (9) is oriented parallel with the axis of the tray. A sealant is employed to ensure that the contents of the cell do not leak between air electrode and the tray (2). A metal electrode (6) such as a zinc negative electrode and an electrolyte are located within the tray (2) interior and electronically isolated from the air electrode. A collapsible foam support (5) is used to accommodate a change in dimension of the metal electrode. Positive and negative terminals (13, 14) are affixed to the ends of the substantially cylindrical container (40) to create the cell (70).</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NQ	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

"Collapsing Foam Anode Backing for Zinc-Air Battery"

5

BACKGROUND OF THE INVENTION

The present invention relates to metal-air cells or batteries, such as zinc-air, aluminum-air, magnesium-air, and lithium-air cells. These cells are advantageous because, among other things, they have high specific energies. The zinc-air electrochemical couple has the highest specific energy, up to 450 Wh/kg, of all commercially available battery systems. Furthermore, the zinc-air system is inherently safe. Both of its electrodes are benign; the negative electrode is composed primarily of innocuous zinc metal, and the positive electrode is composed of a carbon-PTFE (polytetra-fluoroethylene) air cathode.

Currently the most popular configuration for the zinc-air system is the button cell. Zinc-air button cells dominate the hearing aid market because of their high energy density, which is twice that of the competitive mercuric oxide and silver oxide cells. To date other uses for zinc-air cell have been limited to specialized applications, such as oxygen getters for wine (as disclosed in U.S. Patent No. 4,838,442), and 8.4 volt medical telemetry batteries (which consist of a stack of six button cells in a plastic case). Taken together these uses represent a small portion of the total world market for primary batteries, which is dominated by the AAA, AA, C and D cell sizes. These cells (AAA, AA, etc.), which are typically cylindrical and commonly employ carbon-zinc and alkaline manganese dioxide chemistries, have widespread applications in the fields of consumer and industrial electrical and electronic products, ranging from toys and flashlights to pocket pagers and medical telemetry equipment.

During the past 30 years battery developers have attempted to apply zinc-air cell chemistry to a cylindrical battery configuration which would be interchangeable with the popular consumer batteries discussed above. These attempts

have generally employed circular, concentric designs, i.e. those in which the air cathode is cylindrical and located inside an annular zinc anode (see, for example, U.S. Patents 2,938,064; 3,124,487; 3,682,706; 3,881,959; 4,341,847; and 4,491,624) or located outside a central anode cylinder (see, for example, U.S. Patents 3,871,920; 4,009,320; 4,211,830; 4,214,044; and 4,303,743). None of these approaches has been successfully applied to a commercial zinc-air cylindrical cell product.

A common difficulty associated with primary and secondary metal-air cells, such as the zinc-air cell, is expansion of the metal electrode during discharge. When the metal is oxidized to a metal oxide (e.g. zinc oxide) during discharge, it remains in the anode as a second solid phase. The uptake of oxygen atoms adds volume as well as mass to the electrode because the oxide density is generally lower than the metal density. In the zinc electrode, the anode expands by approximately 20% during discharge. If an expansion space is not provided within the cell, the expanding anode mass may cause bulging or rupturing of the cell and leakage of electrolyte, both of which are highly undesirable. If an expansion space is provided, good contact between the electrodes and the electrolyte is not guaranteed. One proposed solution to the expansion problem (presented in U.S. Patent No. 4,894,295 to Cheiky) would employ a diaphragm built into the bottom of the cell container, adjacent to the metal electrode. During discharge, the bottom of the container, which is concave upward, would be pushed downward by the expanding anode, thus accommodating the extra volume. However, this approach involves a complicated product design which is constrained to case materials and thicknesses which allow such expansion.

SUMMARY OF THE INVENTION

The present invention provides a simple and effective means for accommodating a volume change in a metal electrode during charge or discharge, thus avoiding bulging or rupture of the cell container. It accomplishes this at a very low internal cell pressure, thus minimizing the likelihood of

electrolyte leakage from the cell. This invention also provides a durable, long-life metal-air cell that is interchangeable with commercial cylindrical and prismatic cells and batteries.

5 One aspect of the invention is recognition that two factors have hindered the commercial success of metal-air prismatic and cylindrical batteries. First, the air electrode, which is a thin sheet or layer of compressed PTFE-bonded carbon paper, is very difficult to adapt to a curved geometry.
10 Second, the air electrodes are usually not reliably sealed to the cell container (typically the anode can) to prevent electrolyte leakage.

 One metal-air cell of the present invention includes a substantially cylindrical or square sidewall having a region
15 at which an air electrode is mounted. The air electrode is a substantially flat sheet that is parallel to the container axis. This design has the advantage of employing a noncylindrical air electrode which imparts durability not available in prior designs. A sealant is employed to ensure
20 that the contents of the cell do not leak between the air electrode and the container sidewall. A metal electrode such as a zinc negative electrode together with an electrolyte are located within the container interior and are electronically isolated from the air electrode. A collapsible foam support is
25 located within the anode compartment to accommodate a change in dimension of the metal electrode. Positive and negative terminals are affixed to the ends of the container to create the battery.

 In a preferred embodiment of the present invention,
30 the metal-air battery includes a prismatic anode tray typically made of a plastic resin which is chemically stable in the alkaline electrolyte. The bottom of the tray has one or more holes in it which are covered by a porous hydrophobic membrane to prevent electrolyte leakage. A sheet of collapsible closed
35 pore foam is placed on top of the porous membrane, to accommodat the expansion of the electrode during discharge. The holes in the bottom of the tray permit the gases contained

within the pores of the foam to escape, thus minimizing pressure buildup in the cell.

In the preferred embodiment, the cell tray is surrounded by non-conducting tube to give the cell an overall cylindrical shape. The cell may additionally include an air diffuser mounted on the outside of the air electrode. In a further preferred embodiment, the tray or container, the air electrode, and the cell terminals are surrounded by a shrinkable tube which is shrunk around the cell contents to form a leak-proof seal.

The metal electrode of the cell will sometimes include zinc metal powder suspended in a gelled alkaline electrolyte. The resilient foam support employed in this invention is typically located between and touching the gelled electrolyte/metal electrode and the container or tray bottom. Most preferably, the foam support is a closed-cell polyethylene material.

The present invention employs a simple and inexpensive method not available in previous diaphragm designs for accommodating electrode volume change. Other features and advantages of the invention will appear from the following description in which the preferred embodiment is set forth in detail in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a zinc-air battery according to a preferred embodiment of the invention.

FIG. 2 is a perspective view of a battery container according to a preferred embodiment of the invention.

FIG. 3 is a perspective view of an air electrode assembly according to a preferred embodiment of the invention.

FIG. 4 is a diagrammatic, cross-sectional illustration of a zinc-air cell constructed according to a preferred embodiment of the invention.

FIG. 5 is a cross-sectional view of another embodiment of a battery; having a resilient foam support between the cell container and the metal electrode.

FIG. 6 is a graphical comparison of the discharge characteristics of a commercial AA cell and a zinc-air cell of the present invention.

5

DESCRIPTION OF THE PREFERRED EMBODIMENT

Fig. 1 displays a metal-air cell of a type contemplated by the present invention. A cell 70 includes a semi-cylindrical container 40 which forms an outer surface for much of the battery. A resilient foam support 62 and a metal electrode/electrolyte paste 60 are located within the container 40. The foam support 62 is disposed between and touching the container 40 and the electrode/electrolyte paste 60. During use, the foam support 62 is collapsed to accommodate the volume change commonly associated with metal electrodes undergoing charge or discharge. If cell is to be taken through repeated charge and discharge cycles, the foam support should be sufficiently resilient to follow the repeated changes in dimension. An air electrode assembly including an air electrode 48 and an L-shaped current collector 50 is bonded to the container 40 such that the assembly is in electrolytic contact with the metal electrode-electrolyte paste 60. To prevent electrical shorting between the electrodes, while permitting electrolytic contact, a separator 52 is located between the air electrode assembly and the metal electrode. Current collector 50 (associated with the air electrode) includes a flap 66 which is affixed to and in electrical contact with positive terminal 56. The flap 66 is oriented perpendicular to the main body of air electrode current collector 50. An insulator 58 separates the left side of container 40 which is negatively charged from the positively charged flap 66 of the air electrode current collector. Negative terminal 64 is affixed to and in electrical contact with the battery container 40 which serves as a current collector for the metal electrode. Finally, an air diffuser 54 which distributes oxygen uniformly over the air electrode surface is affixed to the battery assembly at the air electrode surface. The air diffuser is a porous, hydrophobic member which is made of, for example, "G reTex" (registered trademark

of W.L. Gore and Associates of Elkton, Maryland) or "Porex" (registered trademark of Porex Corp. of Fairburn, Georgia).

Fig. 2 displays one type of substantially cylindrical container 40 that may be employed in the present invention.

5 The container may be made of, for example, nickel-plated brass. In the embodiment shown, the container 40 has the shape of a semi-circular trough. The curved bottom (or sidewall) of the container is defined by a radius approximately equal to that of a corresponding cylindrical cell such as an AAA, AA, C or D
10 cell. For an AA cell, the radius of the container 40 is approximately 0.278 inches. The bottom of the container may also be squared off such that its width and height are both approximately 0.545 inches in the case of an AA cell. A battery of this type is referred to as a prismatic battery.
15 Prismatic cells serve the same function as cylindrical cells, and are typically employed in devices having battery compartments with flat, rather than rounded surfaces.

The container 40 shown in Fig. 2 includes a cavity 42 in which the electrolyte and metal air electrode are located
20 and also includes flat sealing rim 44 defining a generally rectangular opening 45. Rim 44 provides a flat surface 47 for sealing the air electrode to the container. The container may also include one or more additional openings to which one or more additional air electrodes are mounted.

25 Fig. 3 shows a perspective view of the air electrode assembly 46 including air electrode sheet 48, separator 52, and current collector 50. The air electrode assembly includes one or more flat regions along its length to provide a surface for bonding to the sealing rim to the battery container. In this
30 way, cell sealing is reduced to the simple and reliable task of bonding the air electrode to the flat sealing rim. The bond may be supplemented by compressive forces exerted by a cell wrapper or label, which is a thin shrinkable plastic tube shrunk tightly around the cell.

35 The air electrode 48 may comprise a thin (typically 0.010 to 0.020 inch s thick), porous she t of PTFE-bonded carbon pressed onto a nickel meshed current collector. Th air

electrode may also be a hybrid electrode such as a combination air and manganese dioxide electrode.

In addition to an air electrode and a current collector, the air electrode assembly will typically require a separator 52 on its active face to prevent electrical shorting to the metal electrode mass. The separator may be made from any porous or semi-permeable structure stable in highly alkaline electrolyte such as an aqueous potassium hydroxide solution. Examples of separator material include 100% polyvinyl alcohol (PVA) papers such as those manufactured by Chicopee Corp. (New Brunswick, NJ) microporous polypropylene such as "Celgard" (registered trademark of Hoescht-Celanese Corp., Charlotte, NC), and radiation grafted polyolefin films such as those manufactured by RAI Corp. (Hauppauge, NY). The separator may be bonded to the air electrode with, for example, a PVA glue to form part of the air electrode assembly. During assembly, however, the separator can be directly bonded to the container as a separate element, independent of the air electrode.

The separator and air electrode, either separately or as a unit, are bonded to the container with a suitable glue, cement, or resin. Examples include asphalt-based cements and polyamide-based cements. These materials are disclosed, for example, in U.S. Patents 3,922,178; 4,740,435; 4,248,944; 4,282,293; and 4,224,736 which are hereby incorporated by reference. In addition, the bonding may be accomplished or augmented with a heat shrinkable tube which surrounds the container and air electrode assembly, or with heat sealing or friction welding.

Metal-air cells of the type shown in Fig. 1 may be assembled by the following steps. First, the layer of collapsible polymeric foam and the metal electrode/electrolyte formulation are placed along the container bottom. Next the air electrode assembly is formed by placing an air diffuser onto the air electrode surface. A positive end cap - typically nickel-plated steel - is joined to the bared screen of the air electrode current collector flap via, for example, soldering or spot welding. The air electrode current collector flap with

the positive end cap is then folded over the end of the cell container or tray, insulated from it by an insulating spacer made of paper or a suitable polymer. A negative end cap - typically nickel-plated steel - is joined to the other end of the container via, for example, soldering or spot welding. Finally, a shrinkable tube (such as a heat shrinkable plastic tube) is placed over this assembly and shrunk to form a tight skin. When shrunk, the tube holds the positive cap in position and compresses the air electrode against the container forming a seal. The tube should have holes or other air permeable means fluidly coupled with the air diffuser to allow oxygen into the cell. Alternatively, the shrinkable plastic tube may have an air diffuser incorporated into its structure.

Figure 4 shows a preferred metal-air cell of the present invention. The cell includes a plastic or metal tray (container) 2 having a top, left and right end walls, and a circumferential sidewall. The circumferential sidewall includes a substantially flat bottom having one or more air holes 3. The terms "left," "right," "top," and "bottom" are used merely for convenience, to identify opposite sides of tray 2. These holes are sealed against external leakage of electrolyte by a porous hydrophobic membrane 4, which is bonded along its periphery to the interior of the tray bottom. A collapsible foam 5 is superposed with respect to the membrane, and a metal electrode 6 rests on the foam. When the cell is discharged the foam is compressed by the expansion of the metal electrode, and the gases in the pores of the foam exit the cell through the holes in the tray, thereby minimizing pressure buildup. Electrical contact to the metal electrode is made via a current collection nail 7, in combination with a conductive screen 8, to which it is conductively attached. An oxygen electrode 9 and a porous separator 10 are bonded to the top rim of the tray with a suitable cement, heat sealing, or friction welding at junctions 11a and 11b. Electrical contact to the oxygen electrode is via screen 12, which is conductively attached to the oxygen electrode 9. The cell also has a conductive positive end cap 13 and conductive negative end cap 14 conductively bonded to the screen and nail, respectively.

The cell may be inserted into a non-conducting tube (not shown) with an external diameter and length equal to that for a conventional cylindrical cell.

The foam support provides an electrolyte-impervious base onto which the metal electrode-electrolyte paste is placed during cell assembly, and which holds the metal electrode in position against the separator and air electrode. As the battery is discharged, the metal electrode expands against the support, gradually collapsing it. If the battery is to be rechargable, a resilient foam (one that can expand and contract with the negative electrode) should be employed.

A preferred support foam is a closed pore polyolefin material, such as "Volara" (registered trademark of Voltek Corp. of Japan). Polyolefins are particularly inert and non-contaminating in the presence of the electrolyte (typically a solution of potassium hydroxide and water), and the closed pore structure prevents absorption of electrolyte by the foam, which would degrade cell performance. The foam should preferably have properties that permit the collapsing to occur at a minimal pressure. This avoids the problems of pressure-induced bulging and leakage of the electrode and electrolyte. It has been found that a single layer of Volara about 0.094" thick, with a density of 2 pounds per cubic foot, will provide the required expansion volume, and at a minimal collapsing pressure, for cells displacing approximately the same volume as cylindrical AA cells. For smaller and larger cells the number of layers and surface area of the foam insert must be varied accordingly.

As noted, the electrolyte may be a gelled alkaline aqueous solution such as gelled potassium hydroxide. In general, the metal electrode may be a powder or fine grain metal such as zinc, magnesium, aluminum, alloys of these, or other suitable metal electrode materials known in the art. For a zinc electrode, the metal electrode/electrolyte material is preferably a blend of battery grade zinc powder, potassium hydroxide electrolyte and a gelling agent which forms a paste similar to that used commercially in alkaline manganese dioxide cells. The metal electrode formulation may be adjusted by

means well known in the art to optimize cell performance for a particular application, e.g., low drain, high drain, or general purpose.

5 The membrane 4 may be a porous hydrophobic polymer film such as Celgard 2400 (Celanese Corporation) or Goretex (W.L. Gore & Associates, Elkton, MD). It may be sealed against leakage along its periphery with asphalt-based or polyamide-based cement, or heat sealed or friction welded.

10 During assembly of a cell as shown in Fig. 4, the cell tray bottom is lined with hydrophobic barrier membrane 4, which is sealed along its periphery to be leaktight. The collapsible foam 5 is then inserted, followed by the zinc electrode/electrolyte 6 (potassium hydroxide/water/gelling agent) blend. The oxygen electrode 9 and separator 10 are then
15 bonded to the top rim of the tray 2. The current collector nail 7, is then inserted through the tray wall and sealed in place. If desired, metal screen 8 is used in conjunction with the nail, and placed on top of the foam and conductively joined (e.g. soldered or spot-welded) to the nail prior to addition of
20 the electrode/electrolyte blend. The current collector screen 12 is then conductively joined to the oxygen electrode 9. The screen may be further conductively attached to a positive cap 13 on the end of the cell, opposite the nail which can similarly be conductively attached to a negative end cap 14,
25 and the entire assembly may then be inserted into a plastic tube.

The completed cell may be provided with a removable moisture proof adhesive or heat sealed protective tape placed
30 over the portion of the cell that is to be accessible to the air. This is desirable for cells which are sold in bulk or in packages which do not provide protection from water gain or loss in storage. In addition, when cells are sealed in this manner less expensive materials can be used for final packaging.

35 Alternatively, the cells may be sealed by packaging in a porous clear blister and card packag . In this configuration automatic removal of the protective tape will occur when the package is opened. This design will incorporate

a section of tap into the seal between the blister and the card. A similar process is described in U.S. patent 4,838,422 which is hereby incorporated by reference. Another option for packaging unsealed cells employs a moisture proof pouch or a moisture proof clear blister and card package.

A further aspect of the invention involves the use of a resilient foam support in systems other than the traditional cylindrical batteries described above. For example, button cells and plate and frame batteries may profitably employ a resilient foam support. Figure 5 displays a button-type or prismatic electrochemical cell 101 according to this aspect of the invention. A support tray 105 will be cylindrical if the cell is to be a button type. If, on the other hand, the support tray 105 has one or more flat sides in addition to the bottom side, then the cell will be prismatic. Examples of currently commercialized button cells include zinc anode batteries manufactured by, among others, Rayovac, Eveready, and Duracell. Prismatic zinc-air batteries are currently made by Cegasa of Vitoria, Spain, and under development by DEMI of Santa Barbara, California, and Air Energy Resources, Inc. of Smyrna, Georgia. In each case, the battery employs a primary cell having a zinc metal powder anode suspended in a gelled alkaline electrolyte.

As shown in Fig. 5, a collapsible polymeric foam support 107 is located in the bottom of support tray 105. Directly on top of the foam support is a metal electrode 102 and associated metal electrode current collector 106. An air electrode 103 is located on top of the support tray 105 and separated from the metal electrode by a separator 104. The container 105 may be made from a metal or polymeric material. The current collector 106 carries the electrical current generated from the chemical reaction at the metal electrode to the battery container, where it may be fixedly attached to a metal case via, for example, spot welding or soldering, or fixedly attached to a feedthrough means which exits a polymeric case. The current collector may be made from expanded copper or brass film or foam for alkaline zinc electrodes, for example.

Example

A prismatic zinc-air cell approximately 0.545 inches square and 2.00 inches long (approximately equal to the diameter and length, respectively, of a AA alkaline cell) was constructed as follows:

An anode tray upper portion was machined from a block of solid acrylic plastic sheet stock to obtain side and end walls 0.500 inches high by 0.04 inches thick, with a 0.125 inch wide by 0.040 inch thick rim around the perimeter of the top opening and an open bottom.

The tray bottom was cut from a sheet of acrylic plastic 0.04 inches thick, to a width of 0.545 inches and a length of 2.0 inches. Three 0.125 inch diameter holes were drilled through the tray bottom, along the center line of width and equidistant from one another and the ends of the tray bottom.

A 0.545 inch wide by 2.0 inch long piece of gas permeable hydrophobic material (Celgard 2400) was superposed on the tray bottom, which was, in turn, placed firmly and squarely against the bottom edges of the upper portion of the tray, and cemented in place using polyamide cement (Henkel GAX 11-972).

A 0.055 inch diameter pilot hole was drilled through one end of the anode upper tray, followed by a 0.128 inch countersink into which was placed an O-ring (Parker 2-002), into which was inserted a 0.054 inch diameter by 2.00 inch long brass rod, so that it extended through the anode compartment nearly to the opposite end wall. This was the anode current collector.

A 0.465 inch wide by 1.92 inch long by 0.188 inch thick piece of closed cell collapsible plastic material (Volara 2A) was then inserted into the tray and placed snugly against the Celgard lining of the tray bottom interior.

The tray cavity was then filled with a zinc anode consisting of battery grade zinc powder (Overpelt Grade 308, amalgamated with 3% by weight mercury), premixed 70% by weight with a solution of 35% potassium hydroxide in water and 0.6% by weight of a gelling agent (Carbop 1 940). The cavity was

filled so that the upper surface of the zinc anode mixture was flush with the top surface of the anode tray.

5 A 0.420 inch wide by 1.875 inch long piece of separator material (Chicopee 7601) was placed on top of the tray and anode material so that about 0.060 inch of the tray rim was exposed. The exposed portion of the rim was coated with a polyamid cement (Henkel GAXZ 11-972) and then a 0.545 inch wide by 2.00 long piece of air cathode material (Electromedia AE-20) was placed onto the rim and held firmly in place until the cement had set.

10 A 0.500 inch wide by 2.25 inch long strip of cathode current collector material (Delker 0.028 inch thick expanded nickel foil) was placed on top of the air cathode, with the extra length folded over the end of the tray edge opposite that containing the brass anode rod. A 0.500 inch wide by 2.00 inch long piece of 0.040 thick gas permeable hydrophobic open cell material (Porex 4765) was placed on top of the current collector, and the entire tray length was wrapped on all four sides with a piece of 0.005 inch thick adhesive-backed, heat-shrinkable plastic material (Avery Metalized Vinyl-Faced Sheet Stock) 2.00 inches wide by about 2.25 inches long. Material of this type is commonly used for the exterior wrapping of alkaline AA cells. Heat was then applied with a hot air gun to shrink the label tightly around the assembly.

25 The completed cell weighted 0.8 ounces. A comparable conventional AA alkaline cell weighs 0.9 ounces.

The cell was then placed across a 20 ohm resistor and its voltage was recorded versus time until a lower cutoff voltage of 0.9 V was reached.

30 A conventional AA cell (manufactured by Duracell) was then placed across a 20 ohm resistor and its voltage was recorded versus time until the 0.9 V cutoff was reached.

35 The two discharge curves are shown in Fig. 6. The zinc-air cell (solid curve) lasted for 110 hours, versus 32 hours for the conventional AA cell (dotted curve), a multiple of 3.4. Delivered capacity was 6.5 Ah for the zinc-air cell versus 1.8 Ah for the conventional AA cell.

The present invention has now been described in terms of preferred embodiments. As many modifications to the present invention can be envisioned without departing from the essential nature of the invention, the appended claims, which
5 define the invention, should be read in a broad, inclusive sense.

WHAT IS CLAIMED IS:

1. A metal-air cell comprising:
 - a container including a substantially cylindrical
 - 5 circumferential sidewall with an axis and first and second ends, and end walls at the first and second ends, the circumferential sidewall and end walls having inner surfaces defining an interior, a portion of said sidewall defining an air electrode region;
 - 10 a source of oxygen fluidly coupled to the air electrode region;
 - a generally flat air electrode oriented substantially parallel with the axis, the air electrode being fluidly coupled with the source of oxygen, the air electrode sized to cover the
 - 15 air electrode region;
 - a metal electrode located within the container interior;
 - an electrolyte within the container interior;
 - a separator electronically isolating the metal electrode from the air electrode; and
 - 20 a sealant which sealingly mounts the air electrode to the circumferential sidewall so to cover the air electrode region.
2. A metal-air cell as recited in claim 1 further comprising a collapsible foam support disposed against the metal
- 25 electrode.
3. A metal-air cell as recited in claim 1 wherein the circumferential sidewall has an average radius of at least 0.25 inches.
- 30
4. A metal-air cell as recited in claim 1 wherein the air electrode region comprises an opening into the interior.
5. A metal-air cell as recited in claim 4 wherein the air
- 35 electrode region further comprises a flat rim surrounding the opening.
6. A metal-air cell comprising:

a tray including a circumferential sidewall including a bottom having one or more air holes, an air electrode region, first and second ends, and end walls at the first and second ends, the circumferential sidewall and end walls having inner surfaces defining an interior;

a source of oxygen;

an air electrode fluidly coupled with the source of oxygen, the air electrode sized to substantially cover the air electrode region;

a metal electrode located within the tray interior;

a hydrophobic membrane covering the one or more air holes;

a separator electronically isolating the metal electrode from the air electrode; and

a sealant which sealingly mounts the air electrode to the tray so to cover the opening.

7. A metal-air cell as recited in claim 6 further comprising collapsible foam support disposed against the metal electrode.

8. A metal-air cell as recited in claim 6 additionally comprising an a non-conducting tube surrounding the tray.

9. A metal-air cell as recited in claim 6 wherein the metal electrode comprises zinc metal powder suspended in said electrolyte, said electrolyte being a gelled alkaline electrolyte.

10. A metal-air cell as recited in claim 6 further comprising a shrinkable tube surrounding the cell.

11. An improved metal-air cell of the type typically including a metal electrode, an air electrode, a separator, and an electrolyte within a container, the improvement comprising:

the container including a substantially cylindrical circumferential sidewall with an axis and first and second ends, and end walls at the first and second ends, the circumferential sidewall and end walls having inner surfaces

defining an interior, a portion of said circumferential sidewall defining an air electrode region;

a generally flat air electrode oriented substantially parallel with the axis, the air electrode sized to cover the
5 air electrode region;

a sealant which sealingly mounts the air electrode to the circumferential sidewall so to cover the air electrode region.

12. A metal-air cell comprising

10 a container including one or more sidewalls of which at least one includes one or more air holes, an air electrode region, first and second ends, and end walls at the first and second ends, the sidewalls and end walls having inner surfaces defining an interior;

15 a generally flat air electrode sized to cover the air electrode region;

a metal electrode located within the container interior;

an electrolyte within the container interior;

means for supplying oxygen to the air electrode;

20 means for electronically isolating the metal electrode from the air electrode; and

means for sealingly mounting the air electrode to the container so to cover the air electrode region.

25 13. An improved cell of the type typically including two electrodes, a separator, and an electrolyte within a container, the improvement comprising

a metal electrode having an electrode surface, said metal electrode being of a type which changes a first dimension
30 during charge or discharge; and

a collapsible foam support having a support surface disposed between and touching the electrode surface and the container, wherein the resilient foam surface changes a second dimension in response to a change in the first dimension of the
35 metal electrode.

14. A cell as recited in claim 13 wherein the foam support is situated between and touching the electrode surface and the container.

5 15. A cell as recited in claim 13 wherein the foam support is an insulator.

16. A cell as recited in claim 13 wherein the foam support is a closed-cell foam.

10 17. A cell as recited in claim 13 wherein the foam support comprises polyethylene.

15 18. A cell as recited in claim 13 wherein the metal electrode is a zinc electrode.

19. A cell as recited in claim 13 wherein the metal electrode comprises a zinc metal powder suspended in a gelled alkaline electrolyte.

20 20. A cell as recited in claim 13 wherein the metal electrode is a aluminum electrode.

25 21. A cell as recited in claim 13 further comprising a current collector disposed between the metal electrode and the foam support.

22. A cell as recited in claim 13 wherein the cell is button cell.

30 23. A cell as recited in claim 13 wherein the cell is a prismatic cell.

35 24. A cell as recited in claim 13 wherein the container includes a section of said container adjacent to the foam support, said section comprising one or more air holes.

25. A cell as recited in claim 24 further comprising a hydrophobic membrane situated between and touching the foam support and the one or more holes.

5 26. A method for accommodating a change in dimension of an electrode including the steps of

charging or discharging a cell, the charging or discharging causing a first dimension of the electrode to change; and

10 supporting a surface of the electrode with a collapsible foam support, wherein the collapsible foam support changes a second dimension in response to a change in the first dimension of the electrode.

15 27. A method as recited in claim 26 wherein the charging or discharging is carried out on a zinc electrode.

28. A method as recited in claim 26 wherein the supporting step carried out using a closed-cell polyethylene foam.

20 29. A method as recited in claim 26 further comprising a step of allowing gas from the resilient foam support to escape from the cell.

2/3

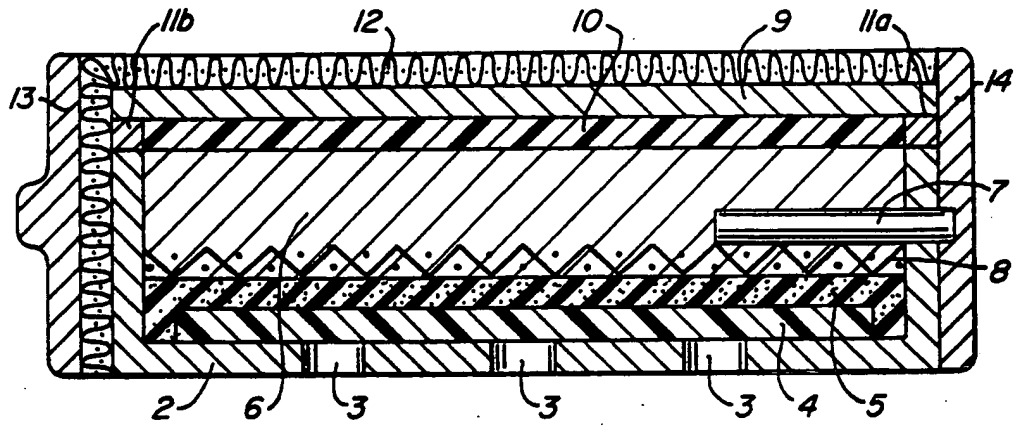


FIG. 4.

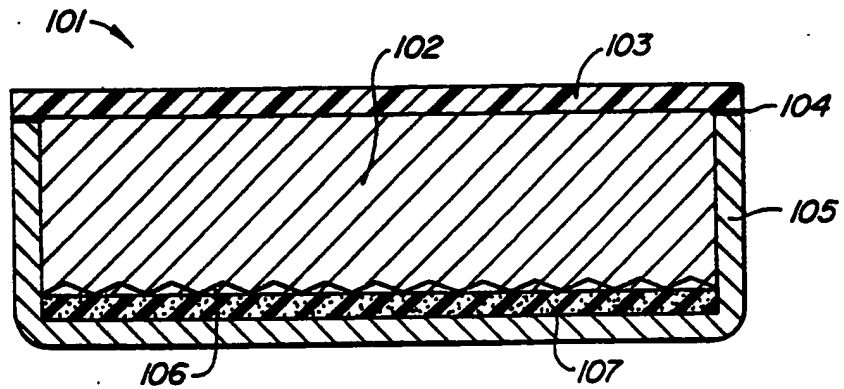


FIG. 5.

3/3

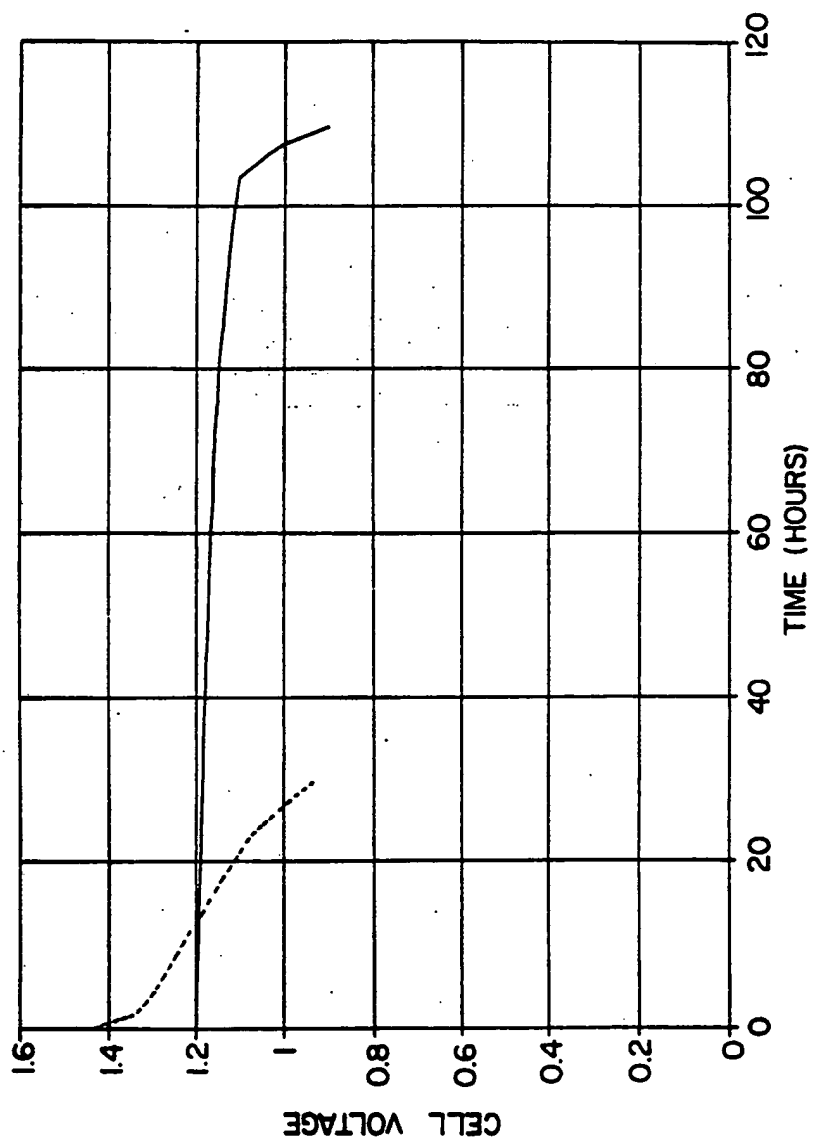


FIG. 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10817**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : H01M 12/06

US CL : 429/27, 66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/72, 82, 86, 163, 54, 55, 57; 429/27, 66

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,855,000 (Jammet) 17 December 1974 See Fig. 1, See col. 1, lines 52-56	1-5, 11-19
Y	US, A, 4,404,266 (Smilanich) 13 September 1983 See col. 4, lines 11-17	6-10, 20-29
Y	US, A, 4,054,726 (Saner et al) 18 October 1977 See col. 1, lines 14-20 and col. 1, line 65 - col. 2, line 7.	6-10, 20-29
Y	US, A, 4,687,714 (Oltman et al) 18 August 1987 See Abstract	6-10, 20-29
Y	US, A, 3,598,655 (Hamlen et al) 10 August 1971 See col. 2, lines 48-52	6-10, 20-29

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

26 FEBRUARY 1993

Date of mailing of the international search report

16 MAR 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

ANTHONY SKAPARS

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-2773